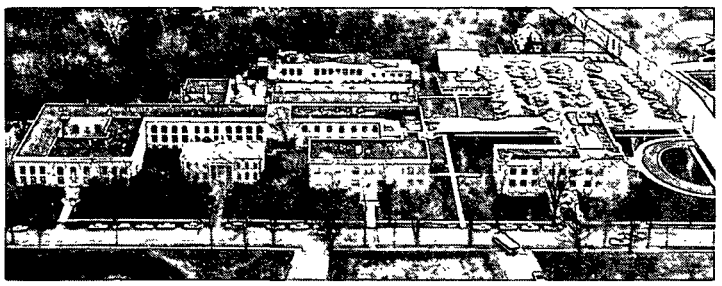

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REGIOSELECTIVE ALKYLATING OF ANTHRAHYDROQUINONE AND ANTHRONE IN WATER WITH QUINONEMETHIDES AND OTHER ALKYLATING AGENTS

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MARCH, 1981

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The Institute of Paper Chemistry, Appleton, WI. 54912

GENERAL SUMMARY

The work described herein was taken from data generated from IPC Project 3475-2 (formerly 3370), which is entitled "Reactions of Pulping and Bleaching - Delignification Reactions," and has been submitted to the Journal of Organic Chemistry for publication. The project is concerned with developing a fundamental understanding of the chemistry of delignification. Toward this goal, we have been examining the reactions of ligninlike intermediates (quinonemethides, QM) with anthrahydroquinone (AHQ), the reduced form of anthraquinone (AQ), in an attempt to explain the increased delignification rates that have been observed during AQ pulping.

Quinonemethides are produced from lignin during pulping and are believed to be a focal point in the chemistry of lignin fragmentation and condensation reactions. Since AHQ promotes fragmentation reactions and retards condensation reactions of lignin models, it is likely that AHQ interacts with quinonemethides.

This paper describes products which we have isolated in high yields from the reaction of some simple QMs with AHQ. Proof of structures was accomplished by detailed spectral studies, principally involving proton and carbon-13 NMR. The study was extended to include several reactants, besides QMs, in order to determine the reactivity of AHQ in pulping systems. Hopefully, this information will lead to improved methods of lignin removal.

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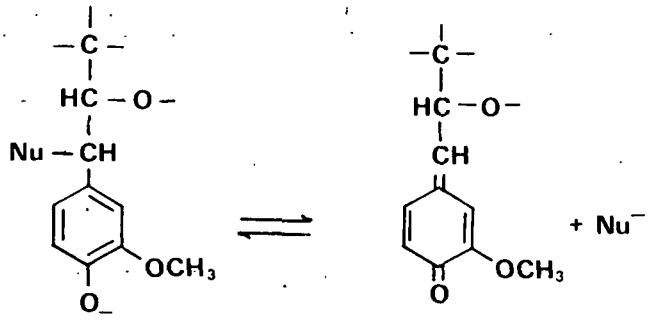
Anthrahydroquinone (AHQ) and anthrone are alkylated in the C-10 position by quinonemethides, generated in situ from p-acetoxybenzyl chlorides, to give adducts 13-15, 24, 25, 28, 29 and 32. Aqueous alkylations of AHQ with methyl vinyl ketone, cinnamaldehye and benzyl chloride also produces C_{10}-substituted 10-hydroxyanthrones. Simple ketones and aldehydes do not, however, alkylate AHQ in aqueous alkali. The spectral characteristics of the adducts indicate that the C_{10}-substituent exists (at least partially) folded over the plane of the anthrone ring skeleton. The carbon-13 NMR spectra are discussed in detail.

A critical step in the making of paper from wood by an alkaline pulping process is the efficient removal of one wood component, lignin, without destroying too much of the valuable component, cellulose.[1] Addition of catalytic amounts of anthraquinone (AQ) to alkaline pulping systems causes an acceleration in the rate at which lignin is removed, while increasing the yield of pulp.[2] Considerable interest has developed in the mechanism of how AQ achieves this desirable selectivity.[3-17]

The increase in delignification rate is probably a result of anthrahydroquinone (the reduced form of AQ and abbreviated as AHQ) both promoting cleavage of lignin bonds to produce water soluble lignin fragments[5-8] and retarding the condensation (polymerization) of lignin and/or lignin fragments.[4,5,9,12] Both the lignin fragmentation and condensation reactions are believed[18] to involve quinonemethide (QM) intermediates, represented in abbreviated form by structure 2. During typical alkaline pulping reactions, performed at 170° in water, these lignin quinonemethides should be very short lived due to rapid capture by nucleophiles, such as hydroxide, sulfide, phenoxides and water (eq a).[16]

This report concerns the reactions of anthrahydroquinone dianion, AHQ^{-2}, with several substrates, including some simple quinonemethides, in an attempt to understand the chemistry of alkaline pulping systems containing anthraquinone.



(a)

1 2

RESULTS AND DISCUSSION

Quinonemethides

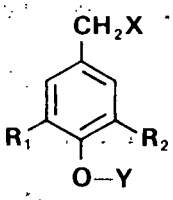
Quinonemethides, even at room temperature, are quite reactive species and are, therefore, generated *in situ*. The most ideal QM precursor would be a *p*-hydroxybenzyl chloride, which when treated with base would liberate a QM. However, these compounds are also not too stable. For example, *p*-acetoxybenzyl chloride (1),[19] upon treatment with acidic-methanol, gave ether 4 rather than the desired transesterification product 5. The reaction was followed by ^{1}H-NMR and gave no evidence of 5 or an intermediate methoxyacetate 6; presumedly 1 hydrolyzed directly to a quinonemethide (9) and the latter was rapidly captured by solvent.

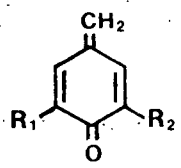
Treatment of 3[19] with pyridine gave a salt 12. The salt could be recrystallized from warm water, but was unstable in either refluxing methanol or aqueous hydroxide, giving rise to 7 and 8, respectively. Consequently, the salt looked to be an ideal candidate for generating a quinonemethide without the interference of a nucleophilic base in the system. Other potential QM precursors were 1-3.

Anthrahydroquinone Dianion

Both AHQ and AHQ^{-2} are rapidly oxidized by air to AQ and consequently their preparation and handling was done in a pure nitrogen atmosphere. The dianion, which is deep red in color, was made by treating AQ with sodium dithionite in

aqueous alkali.[20] Acidification of the solution gave AHQ, a light green, water insoluble solid. The excess dithionite and inorganic salts were washed away by repeated filtrations under nitrogen. Addition of alkali regenerated the red colored AHQ^{-2}. Anhydrous AHQ was obtained by vacuum evaporation of the washed AHQ.





1 X = Cl, Y = Ac, $R_1 = R_2 = H$

2 X = Cl, Y = Ac, $R_1 = H$, R_2 = OMe

3 X = Cl, Y = H, $R_1 = R_2$ = Cl

4 X = OMe, Y = H, $R_1 = R_2 = H$

5 X = Cl, Y = H, $R_1 = R_2 = H$

6 X = OMe, Y = Ac, $R_1 = R_2 = H$

7 X = OMe, Y = H, $R_1 = R_2$ = Cl

8 X = OH, Y = H, $R_1 = R_2$ = Cl

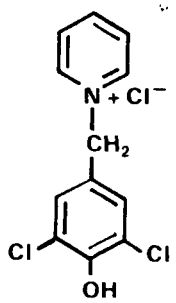
19 X = OH, Y = H, $R_1 = R_2 = H$

20 X = OH, Y = H, $R_1 = H$, R_2 = OMe

9 $R_1 = R_2 = H$

10 $R_1 = H$, R_2 = OMe

11 $R_1 = R_2$ = Cl



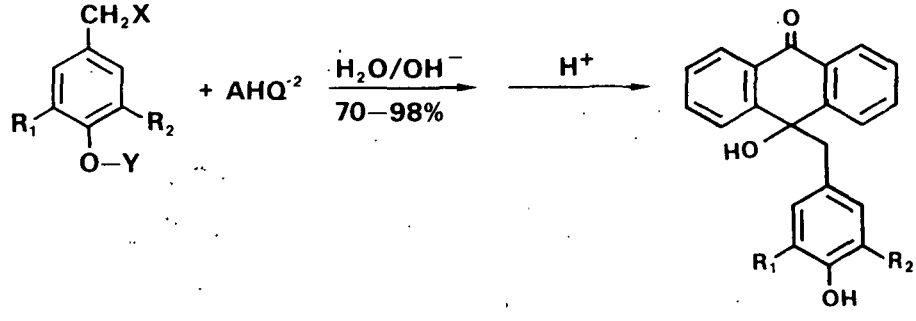
12

QM + AHQ^{-2} Reactions

In an attempt to avoid complications due to competing nucleophiles, we first examined the reaction of pyridine salt 12 with anhydrous AHQ in the presence of dioxane and a trace of pyridine. Work-up of the reaction provided only recovered salt 12 and AQ (from AHQ and air). The lack of reaction may have been due to the insolubility of salt 12 in dioxane, the inability of the salt to enter into an equilibrium which generates QM (and pyridine-HCl) or to a low reactivity of nonionic AHQ. Interestingly, the salt 12, when added to an aqueous solution of AHQ^{-2}, rapidly

discharged the red color. A product was isolated in good yield, which was not the salt's hydrolysis product 8 but, when subjected to gas chromatography, gave rise to 8 and AQ.

This observation led us to examine the reactions of chloroacetate 1 and 2 with AHQ^{-2}. The reactions were conducted in aqueous alkali, where the chloroacetates would be expected to hydrolyze to quinonemethides 9 and 10, respectively. Surprisingly, high yields of 1:1 addition products of QM, and AHQ, and henceforth referred to as QM-AHQ adducts, were isolated. The equation describing these reactions is given by eq b; the starting materials were 1-3 and 12.



(b)

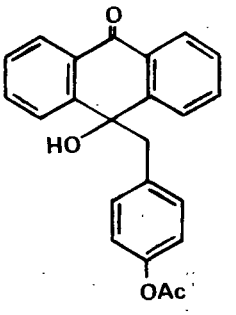
13, $R_1 = R_2 = H$

14, $R_1 = H$, $R_2 = OMe$

15, $R_1 = R_2 = Cl$

STRUCTURE PROOF OF QM-AHQ ADDUCTS

The proof of structures for adducts 13-15 was based on elemental analysis (Table I) and spectral data for the three compounds and two derivatives of adduct 13. The infrared spectra, for example, clearly indicated the presence of hydroxyl and diaryl ketone functional groups. Acylation of 13 under mild conditions gave a monoacetate (16); more strenuous conditions gave a diacetate (17).



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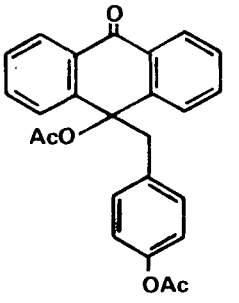


17

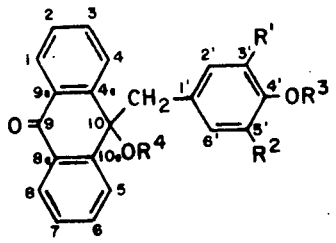
A detailed analysis of the ^{1}H and ^{13}C-NMR spectra (Tables I and II) of the adducts and the two acetate derivatives strongly indicated that the structure of the adducts was that of a 10-benzyl-10-hydroxyanthrone. Run in DMSO as the solvent,[21] the adduct ^{1}H-NMR spectra displayed hydroxyl signals at 8.5-9.7 δ (phenolic) and 6.4-6.5 δ (dibenzylic), both of which exchange with addition of D_2O. The ^{13}C-NMR spectra show only two aliphatic signals, a singlet at about 73 ppm and a triplet at about 55 ppm.

The assignment of the signals in the ^{13}C-NMR spectra was based on a comparison to the published spectra of anthraquinone[22-24] and anthrone 27[22,25] and the observed shifts which occurred upon acylation of the C-10 hydroxyl group. A change at C-10 should affect the benzyl carbon and carbons 4, 4a, 10, 10a and 5 more than the other carbons (the numbering is given in Table I). The ^{13}C-NMR spectra are discussed in a later section.

The proton NMR spectrum of the diacetate derivative was quite informative. The C-1, C-8 protons were shifted far enough downfield to be seen as a doublet; the other six anthrone protons have the expected chemical shifts. Two types of acetate methyl signals, indicative of an aliphatic and aromatic acetate, were observed. The benzyl protons were seen downfield, probably because of the closeness to the C-10 acetoxy group. The IR spectrum of the diacetate also shows both aliphatic and aromatic acetates.

TABLE I

^{1}H-NMR SPECTRAL ASSIGNMENTS AND ELEMENTAL ANALYSES FOR THE QM-AHQ ADDUCTS



NMR SPECTRAL DATA

Solvent	DMSO	DMSO	DMSO	$CDCl_3$	$CDCl_3$	$CDCl_3$
R^1	H	Cl	OCH_3		H	H
R^2	H	Cl	H		H	H
R^3	H	H	H		Ac	Ac
R^4	H	H	H		H	Ac
Phenolic OH	9.00_1^s	9.70_1^s	8.54_1^s	5.44_1^s		
Aliphatic OH	6.40_1^s	6.52_1^s	6.46_1^s	2.98_1^s	3.00_1^s	
C_1-C_8 protons	$7.4\text{-}8.1_8^m$	$7.4\text{-}8.1_8^m$	$7.4\text{-}8.1_8^m$	$7.2\text{-}7.9_8^m$	$7.2\text{-}8.1_8^m$	$7.2\text{-}7.6_6^m$, $8.12_2^{d,J=8Hz}$
C_2' proton	$6.16_2^{d,J=9Hz}$	5.90_2^s	5.32_1^m	$5.42_1^{d,J=1Hz}$	$6.58_2^{d,J=9Hz}$	$6.63_2^{d,J=9Hz}$
C_6' proton			$6.18_1^{d,J=9Hz}$	$6.40_1^{d,J=9Hz}$		
C_3' proton	$5.68_2^{d,J=9Hz}$				$6.13_2^{d,J=9Hz}$	$6.15_2^{d,J=9Hz}$
C_5' proton			5.32_1^m	$5.66_1^{d\ of\ d}$		
$-CH_2-$	3.06_2^s	3.08_2^s	3.08_2^s	3.09	3.12_2^s	3.34_2^s
Other			3.20_3^s	3.34_3^s	2.16_3^s	2.16_3^s, 2.19_3^s

ELEMENTAL ANALYSES

Calc. %C	79.75	65.45	76.30	77.09	75.00
Obs. %C	79.30	65.29	75.86	77.08	75.17
Calc. %H	5.06	3.64	5.20	5.03	5.00
Obs. %H	5.13	3.69	5.90	5.11	5.07

[a] Superscript on the assignments refers to splitting pattern, s = singlet, d = double, t = triplet, q = quartet, m = multiplet; the subscript on the assignments refers to relative integrated area of the signal; the J value refers to the coupling constant.
[b] All signals are reported in PPM (δ) units, relative to TMS.

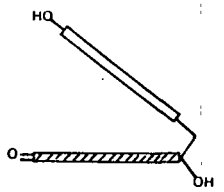
TABLE II

^{13}C-NMR SPECTRAL ASSIGNMENT FOR THE QM-AHQ ADDUCTS[a]

Solvent	DMSO	DMSO	DMSO	$CDCl_3$	$CDCl_3$
R^1	H	Cl	OCH_3	H	H
R^2	H	Cl	H	H	H
R^3	H	H	H	Ac	Ac
R^4	H	H	H	H	Ac
C_1, C_8	127.7^{d}_{ℓ}	128.0^{d}_{ℓ}	128.0^{d}_{ℓ}	128.4^{d}_{ℓ}	127.7^{d}_{ℓ}
C_2, C_7	126.8^{d}_{ℓ}	127.0^{d}_{ℓ}	127.2^{d}_{ℓ}	127.0^{d}_{ℓ}	126.8^{d}_{ℓ}
C_3, C_6	133.6^{d}_{ℓ}	133.6^{d}_{ℓ}	133.8^{d}_{ℓ}	133.4^{d}_{ℓ}	133.1^{d}_{ℓ}
C_4, C_5	125.3^{d}_{ℓ}	125.6^{d}_{ℓ}	125.2^{d}_{ℓ}	126.2^{d}_{ℓ}	123.8^{d}_{ℓ}
C_{8a}, C_{9a}	130.8^{s}	131.1^{s}_{m}	131.4^{s}_{w-m}	132.6^{s}_{w}	130.7^{s}_{w}
C_{4a}, C_{10a}	148.0^{s}_{m}	(147.8^{s}_{m})	$[148.3^{s}_{m}]$	147.2^{s}_{w}	143.4^{s}_{w}
C_9	182.4^{s}_{w}	182.6^{s}_{w}	183.0^{s}_{w}	183.4^{s}_{w}	181.8^{s}_{w}
C_{10}	73.0^{s}_{m}	72.6^{s}_{m}	73.2^{s}_{m}	73.8^{s}_{w}	79.0^{s}_{w}
$-CH_2-$	54.8^{t}_{w-m}	53.9^{t}_{m}	55.3^{t}_{m}	54.8^{t}_{m}	52.7^{t}_{m}
C_1'	125.1^{s}_{m}	128.4^{s}_{m}	125.4^{s}_{m}	131.3^{s}_{w}	130.2^{s}_{w}
C_2', C_6'	130.8^{d}_{ℓ}	130.2^{d}_{ℓ}	114.2^{d}_{m}, 122.8^{d}_{m}	131.4^{d}_{ℓ}	131.7^{d}_{ℓ}
C_3', C_5'	114.2^{d}_{ℓ}	121.2^{s}_{m}	$[147.0^{s}_{w-m}]$, 114.6^{d}	120.6^{d}_{ℓ}	120.3^{d}_{ℓ}
C_4'	156.0^{s}_{w-m}	(147.8^{s}_{m})	$[145.2^{s}_{w-m}]$	151.0^{s}_{w}	149.4^{s}_{w}
Ester $\diagdown C{=}O$	--	--	--	169.8^{s}_{w}	168.7^{s}_{w}, 168.0^{s}_{w}
CH_3	--	--	55.2^{q}_{m}	21.0^{q}_{w-m}	21.6^{q}_{m}, 21.0^{q}_{m}

[a] Refer to Table III for the nomenclature and meaning of superscripts; the subscripts in this table refer to intensity of the signal; w = weak, m = moderate and ℓ = large, ( ) means only one signal seen for supposedly two carbons, [ ] means assignments could be reversed.

The ^{1}H-NMR spectra of the adducts show some peculiar upfield shifts for the phenolic ring subunit. Ordinarily, phenols show signals in the 6.6-7.0 δ region for the aryl protons. The adducts' corresponding signals are at 5.3-6.6 δ. These upfield shifts suggest that the phenolic rings spend at least a portion of their time in the magnetically shielded region of the anthrone ring, i.e., sandwich structure 18. The upfield shift of the aryl methoxyl group of 14 can be explained in a similar fashion.



18

If the two aromatic systems of the adducts were acting independently, one would expect the ultraviolet spectra to show λ_{max} at 270-280 ($\varepsilon \approx 1,500$) and 257 nm ($\varepsilon$ 25,000), attributed to the phenolic and anthrone subunits.[26] However, the adducts display a single λ_{max} at 272-278 nm (ε 12-13,000), indicative of phenol/quinone charge transfer complexes.[27]

Additional evidence for ring sandwiching was provided by the mass spectra of the adducts. The spectra showed the expected molecular ions and a prominent fragmentation which regenerated AHQ and the corresponding QMs. This fragmentation was not observed when the phenolic hydroxyl group was derivatized to a methyl ether. A logical interpretation of this fragmentation is that the phenolic hydroxyl group resides somewhat close to the anthrone carbonyl group (structure 18) and a hydrogen atom is transferred from the one to the other group during a converted set of bond breakages. The mass spectra of the adducts and derivatized products are discussed in detail elsewhere.[28]

Other QM-AHQ Reactions

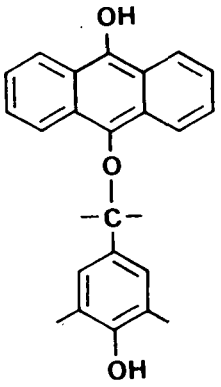
An interesting feature of the adduct formation reactions was that yields were so high, considering the side reactions that are available to the p-hydroxy or p-acetoxybenzyl chlorides and proposed quinonemethide components. All of these would be expected to hydrolyze rapidly in an aqueous alkaline medium to give p-hydroxybenzyl alcohols.[29-31] As an example, the half-life of a simple substituted quinonemethide in neutral methanol at 25° is reported[29] to be 17 seconds. Apparently, the reactions between AHQ^{-2} and simple QMs are very fast.

Adduct formation was poor when benzyl alcohols were used as precursors of quinonemethides. Both p-hydroxybenzyl alcohol (19) and vanillyl alcohol (20) produced adducts (13 and 14) when reacted with AHQ^{-2} at 60°, but the yields were only about 2%; the major products were phenolic condensation products.[28] The poor yields in these cases could be due to: (a) poor QM generation, (b) a greater reactivity between the QMs and phenolate ions in solution, as compared to AHQ^{-2}, and (c) instability of the adducts, which allows the more stable condensation products to build. Concerning this latter point, evidence exists that the adducts enter into an equilibrium with their constituent parts, AHQ and QM, at temperatures of 60° and above.[28]

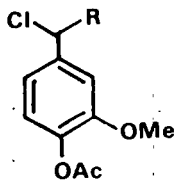
The three adducts discussed so far are all C-10 alkylated anthrone derivatives. The dianion of AHQ has several resonance forms; why didn't alkylation occur at one of these other sites? Could conditions be set up to promote O-alkylation to give an adduct such as 21? The reaction of chloroacetate 1 with AHQ^{-2} has been in several different ways, such as a solvent system of 50% aqueous dioxane and reaction times of 1 minute, and only adduct 13 was obtained (yields > 90%).

The reactions of somewhat hindered chloroacetates 22 and 23 with AHQ^{-2} gave adducts 24 (18%) and 25 (25%), respectively. The low yields appeared to be due to

competing reactions which generate phenolic styrene and polymers thereof. There was no indication of O-alkylated products, such as 21, in the NMR spectra of the crude product mixtures. Consequently, even somewhat hindered alkylating agents still gave C_{10}-alkylation. Crude calculations, based on bond strength and resonance energy data, indicate that a C_{10}-alkylated product should be about 23 kcal/mole more stable than an O-alkylated AHQ derivative.

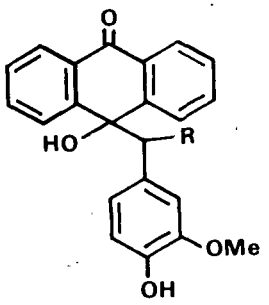


21



22, R = Me

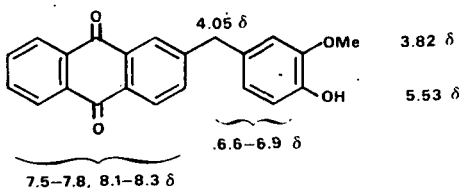
23, R = Et



24, R = Me

25, R = Et

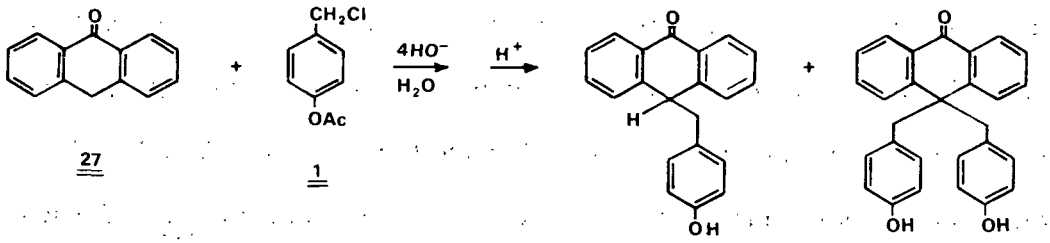
Alkylation of AHQ^{-2} at one of the two side rings should have a higher activation energy than alkylation at C-10 since some aromaticity must be lost during the process. However, if the alkylation reactions are reversible, side ring alkylation may occur under more strenuous conditions, giving rise to a more stable type of product. This fact may account for the appearance of 2-vanillylanthraquinone (26) in wood pulping liquors[32] and alkaline vanillyl alcohol cooks done at 173°C in the presence of AQ.[28] The NMR spectrum of 26 (shown in the figure) displayed no unusual upfield shifts since sandwiching of rings is impossible (according to models).



26

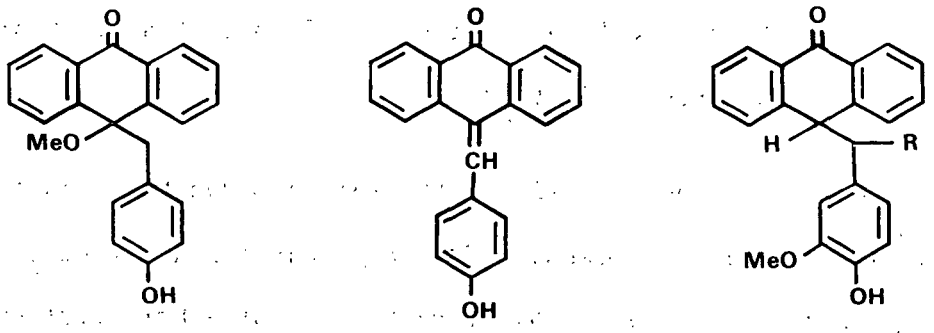
Anthrone, Quinonemethide Reactions

Alkylation of anthrone (27) with chloroacetate 1 in aqueous dioxane containing sodium hydroxide gave a mixture of mono and dialkylated products 28 and 29. Even though a 1:1 ratio of reactants was used, more dialkylated product was formed than monoalkylated product. Apparently, the monoalkylated material is more reactive towards the alkylating agent than is anthrone. Treating anthrone with two equivalents of 1 gave 29 in high yield.



27 1 28 29 (c)

Two other compounds also isolated from the reaction outlined by eq c were anthraquinone and methoxy adduct 30. The production of AQ was a result of the work-up procedure employed. The alkaline solution was exposed to air at the end of the reaction period to precipitate the anthrone as AQ; filtration and acidification afforded the products. No AQ was produced if the work-up was done in a pure nitrogen atmosphere. There is ample literature supporting the autooxidation of anthrone in an alkaline medium to give AQ.[33]



30 31 32

The methoxy adduct 30 was assumed to arise from an autooxidation of 28 before or during attempted methanol recrystallization of the product mixture. Adduct 13 is not a source of 30 since recrystallization of 13 from methanol gave no methanol incorporation. Quinonemethide 31 is also not a logical precursor of 30 since methanol would be expected to add to the methine carbon. Compound 31 was produced from adduct 13 by dehydration with an acid catalyst; it showed no unusual upfield shifts in its NMR spectrum and was surprisingly stable to nucleophiles - it was recrystallized from DMSO/water.

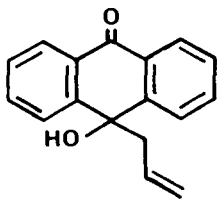
All indications are that monoalkylated anthrone adduct 28 is a sensitive compound. It was isolated in poor yield after several column chromatographies. It decomposed on attempted derivatization with dimethylsulfate in alkaline THF. In contrast, alkylation of anthrone with a slightly bulkier reagent 22 afforded a monoalkylated product 32 which was easy to handle. Treating anthrone with two equivalents of 22 still yields only monoalkylated product. Apparently the formation of dialkylated product is inhibited for steric reasons.

Other Reactions of AHQ^{-2}

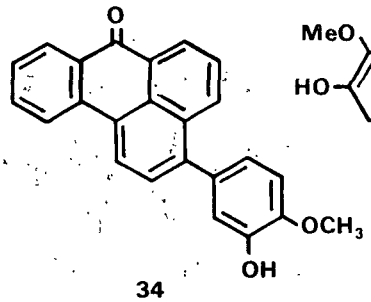
Deshpande[34] reported in 1978 that AHQ^{-2} reacts with allyl bromide to give a C-alkylated product 33. Recently, Fullerton and Ahern[35] have reported that 34, which has been isolated from pulping liquors,[35,36] can be obtained from the reaction of coniferyl alcohol 35 with AQ/glucose; presumably, the C-alkylated derivative 36 is an intermediate in this reaction. We have alkylated AHQ^{-2} with benzyl chloride and obtained a 60% yield of C-alkylated product 37.

The ^{1}H-NMR of 37 showed the same upfield shifts for the aromatic signals noted for the QM-AHQ adducts (Table III). Deshpande[34] notes that the allyl derivative 33 displays upfield vinyl signals in the 4.2-5.2 δ region. A dimethyl allyl derivative is reported to have methyl signals at 0.79 and 1.34, instead of the expected 1.8 δ

region.[34] Apparently, these compounds also exist in sandwich conformations, as explained earlier.



33



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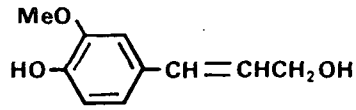
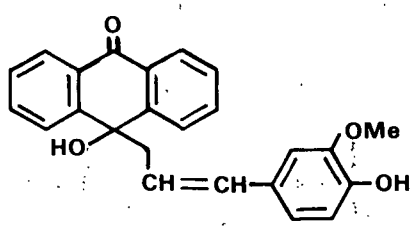
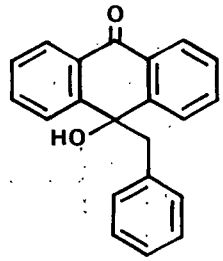


35



36



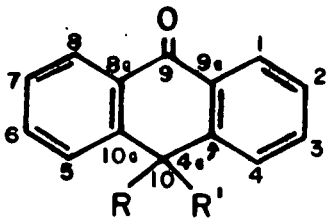
37

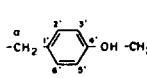
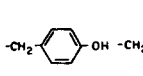
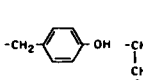
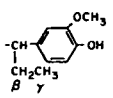
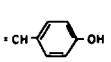
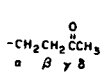
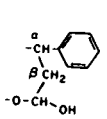
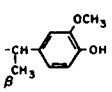
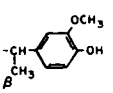
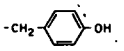
In the pulping of wood a great variety of different organic compounds can be generated, i.e., aromatic ketones and cinnamaldehyde structures from lignin, aliphatic ketones from carbohydrates, etc. Gratzl and coworkers have proposed that AHQ^{-2} may add to lignin carbonyl groups and subsequently cause the fragmentation of lignin.[10] It is important to establish what kind of substrates could interact with AHQ dianion, from the points of view of defining potential pathways by which AQ is lost during pulping and of defining the synthetic utility of AHQ alkylations.

The addition of AHQ^{-2} to a QM is formally a Michael reaction. Other Michael acceptors, which were examined, were methyl vinyl ketone (38) and cinnamaldehyde (39); adducts 40 (54%) and 41 (40%) were obtained, respectively. Based on spectral evidence (Tables III and IV), the methyl vinyl ketone adduct exists as an open structure (40A), while the cinnamaldehyde adduct exists as a mixture of stereoisomers having a closed structure (41B). Both adducts, 40A and 41B, exhibit upfield NMR shifts indicative of some folding of the C-10 substituent over the anthrone ring.

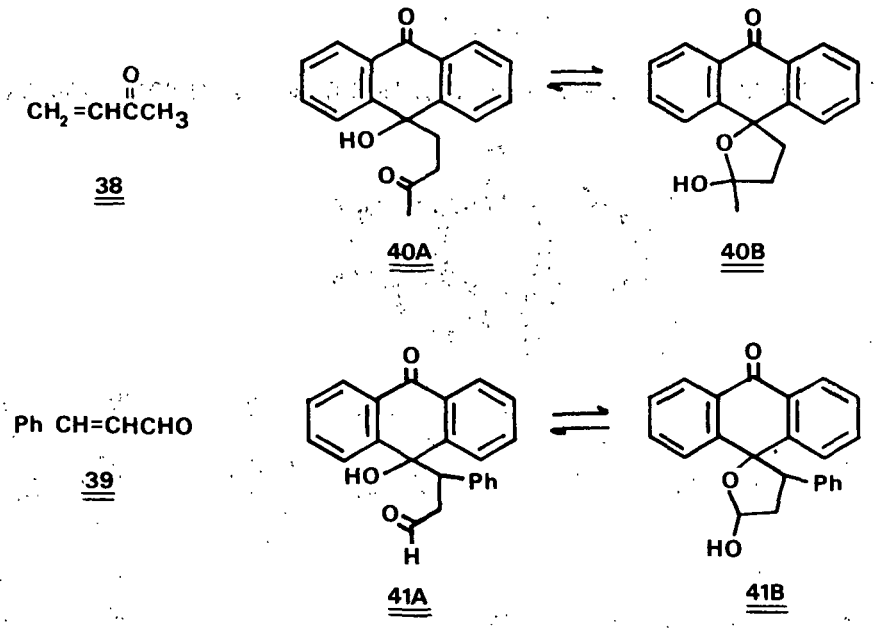
TABLE III

^{1}H-NMR ASSIGNMENTS AND ELEMENTAL ANALYSES FOR SELECTED ANTHRAHYDROQUINONE AND ANTHRONE ADDITION PRODUCTS[a]



TEXT*	30	28	29	25	31	40A	41B	37	24	32
R										
R'	-OCH$_3$	-H		-OH		-OH		-OH	-OH	-H
Positions	PPM	PPM	PPM	PPM	PPM	PPM	PPM[g]	PPM[e]	PPM	PPM
C_1, C_8	7.5-8.0 (m)	7.95 (d)	8.29 (d)	7.4-8.0	7.4-8.3 (m)	7.4-8.1 (m)	8.2 (m)	7.2-8.0 (m)	7.3-8.3 (m)	7.2-8.1 (m)
C_2, C_7		7.4-7.6 (m)	7.84 (t)				7.3-7.8 (m)			
C_3, C_6			7.42 (t)							
C_4, C_5			7.88 (d)							
C_{10}	--	4.72 (t)[b]	--	--	--	--	--	--	--	4.58 (d)
C-α	3.05 (s)	3.12 (d)[b]	3.67 (s)	f	7.4-8.3 (m)	2.0 (m)	2.29 (d of d)	3.16 (s)	3.06 (q)	f
C-β	--	--	--	1.10 (m)	--		2.74 (d of t)	--	1.17 (d)	1.09 (d)
C-γ	--	--	--	0.55 (t)	--	--	3.80 (d of d)	--	--	--
C-δ	--	--	--	--	--	1.82 (s)	6.34 (d)	--	--	--
C_2'	6.18 (d)	6.28 (d)	6.13 (d)	5.34 (s)	7.24 (d)	--	6.1 (d)	6.08 (d)	5.42 (s)	5.81 (d)[c]
C_6'				6.19 (d)		--			6.20 (d)	6.43 (d)
C_3'	5.74 (d)	5.98 (d)	6.00 (d)	--	6.75 (d)	--	6.9 (m)	6.8-7.0 (m)	--	--
C_5'				5.34 (d)		--			5.40 (d)	5.71 (d or d)[d]
C_4'	--	--	--	--	--	--			--	--
Aryl-OH	9.00 (s)	9.03 (s)	9.03 (s)	8.55 (s)	9.77 (s)	--	--	--	8.56 (s)	8.70 (s)
Aliph.-OH	--	--	--	6.34 (s)	--	6.34 (s)		2.62 (s)	6.30 (s)	--
Methoxy	3.36 (s)	--	--	3.24 (s)	--	--	--	--	3.33 (s)	3.40 (s)
ELEMENTAL ANALYSES										
Calc. % C	80.00	84.00	82.76	--	84.60	77.10	80.70	84.00		
Found % C	73.69	81.86	82.28	--	83.76	76.06	80.39	83.95		
Calc. % H	5.45	5.33	5.42	--	4.70	5.83	5.26	5.33		
Found % H	5.13	5.53	5.61	--	4.84	5.71	5.31	5.32		

[a] Values are in δ units relative to TMS = 0; the J values for split signals are in the 7-9 Hz range unless noted otherwise; DMSO-d_6 solvent
[b] J = 5 Hz. [c] J = 1 Hz. [d] J = 1 Hz and 8 Hz. [e] Run with $CDCl_3$ as the solvent.
[f] Unable to locate this signal; it may be under a strong signal.
[g] The α,β and γ protons comprise a ABB'C system with apparent coupling constants for the major isomer of: AB = 13 Hz, AB' = 7 Hz, BB' = 13 Hz, BC = 6 Hz, and B'C = 0 Hz. The relationships and peak assignments for these protons and for the C_2', C_6' ortho aromatic protons were arrived at by decoupling techniques. The OH proton was not seen; there was a large amount of water in our DMSO solvent which may have masked the signal. A spectrum in $CDCl_3$ also did not pinpoint the OH signal. An IR spectrum clearly shows no CHO and the existence of an alcohol.



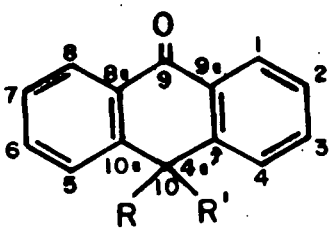
No trace of adducts was observed when AHQ^{-2} was reacted with either acetone (CH_3COCH_3), benzaldehyde (PhCHO), acetovanillone (4-OH-3-OMe-$PhCOCH_3$), benzophenone (PhCOPh), anthrone (27) or ferulic acid (4-OH-3-OMe-$PhCH{=}CHCO_2H$). In fact, no reactions of any type were observed in these cases. Consequently, alkylation of AHQ^{-2} under these conditions by a simple ketone or aldehyde does not lead to a stable product.

The alkylation of AHQ or anthrone anions by p-acetoxybenzyl chlorides was quite efficient. In light of the fact that benzyl chloride also alkylates AHQ dianion, what is the probability that the p-acetoxybenzyl chlorides are reacting as benzyl chlorides (S_N2 mechanism) rather than quinonemethides? Taylor claims that p-acetoxybenzyl chloride (1) reacts with heteroatom nucleophiles via a quinonemethide; this conclusion was reached by comparing the reactivity differences of 1 and meta-acetoxybenzyl chloride, a compound which can not form a QM. We experienced considerable difficulty in preparing m-acetoxybenzyl chloride and, thus, were not able to make a similar comparison study.

Heating adducts of AHQ which have attached p-hydroxybenzyl groups above 60° in an alkaline medium leads to the production of AHQ dianion.[28] However, the simple

TABLE IV

^{13}C-NMR ASSIGNMENTS FOR SELECTED ANTHRAHYDROQUINONE AND ANTHRONE ADDITION PRODUCTS[a]



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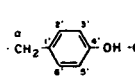
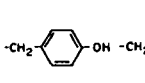
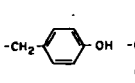
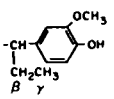
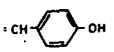
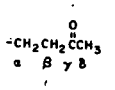
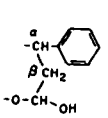
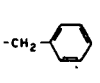
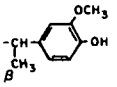
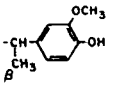
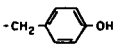
R										
R	-OCH$_3$	-H		-OH		-OH		-OH	-OH	-H
Positions	PPM[b]	PPM[b]	PPM	PPM[b]	PPM[b]	PPM	PPM[b]	PPM[b,d]	PPM[b]	PPM[b]
C_1, C_8	127.0 (d)	128.4	129.0 (d)			127.4 (d)		127.7		
C_2, C_7	126.2 (d)	126.5	127.2 (d)			126.2 (d)		126.2		
C_3, C_6	132.8 (d)	132.2 (d)	133.7 (d)		132.6 (d) 134.2 (d)	133.3 (d)		133.0 (d)		
C_4, C_5	124.7 (d)	125.6	126.4 (d)			125.6 (d)		125.7		
C_{8a}, C_{9a}		131.5 (s)	132.3 (s)		129.3 (s) 131.2 (s)	129.7 (s)		131.0 (s)		
C_{4a}, C_{10a}	147.3 (s)	143.7 (s)	146.8 (s)	144.5 (s) 144.7 (s)	139.8 (s) 135.8 (s)	147.7 (s)	147.6 143.7	146.3 (s)	144.4 (s)	143.3 (s) 142.0 (s)
C_9	181.5 (s)	182.6 (s)	183.1 (s)	181.7 (s)	183.0 (s)	182.6 (s)	182.5	182.4	181.2 (s)	182.9 (s)
C_{10}	72.5 (s)	43.3 (d)	50.0 (s)	74.7 (s)		70.5 (s)	87.2, 85.7[c]	73.8 (s)	74.4 (s)	49.6 (d)
C-α	54.4 (t)	46.6 (t)	48.7 (t)	63.0 (d)		42.5 (t)	59.4, 61.2[c]	55.4 (t)	54.1 (t)	48.3 (d)
C-β	--	--	--	21.6 (t)	--	37.7 (t)	37.5	--	15.4 (q)	17.3 (q)
C-γ	--	--	--	12.6 (q)	--	206.4 (s)	98.6, 100.0[c]	--	—	—
C-δ	—	—	--	--	--	29.3 (q)	--	--	—	--
C_1'		128.3 (s)	127.7 (s)			--		134.2 (s)		
C_2'	130.3 (d)	129.8	130.5 (d)	114.1 (d)	130.6 (d)	--		130.0	112.9 (d)	112.5 (d)
C_6'	130.3 (d)	129.8	130.5 (d)		130.6 (d)	--		130.0	120.8 (d)	120.3 (d)
C_3'	113.6 (d)	113.8 (d)	114.2 (d)	149.2 (s)	115.2 (d)	--		127.2	148.4 (s)	146.1 (s)
C_5'	113.6 (d)	114.6 (d)	114.2 (d)	114.1 (d)	115.2 (d)	--		127.2	113.7 (d)	114.3 (d)
C_4'	155.1 (s)	155.1 (s)	155.1 (s)	145.9 (s)	157.3 (s)	--		126.5	145.4 (s)	144.8 (s)
Methoxy	49.3 (q)	--	--	55.0 (s)	--	--	--	--	54.7 (q)	55.5 (q)

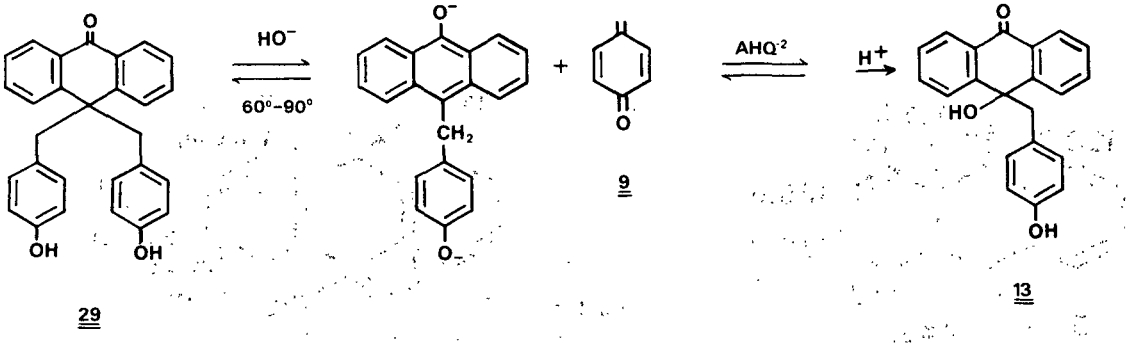
[a] Values are in PPM relative to TMS = 0; DMSO-d_6 solvent

[b] The lack of assignment for the peak position or splitting was due to the complexity of aromatic region, which was either a result of overlapping signals or disymmetry of the molecule or both.

[c] This compound is a mixture of stereoisomer; the first value of the two assignments represents the more intense peak.

[d] The aromatic assignments are quite tentative in this case.

benzyl adduct is stable to these conditions. Therefore, it was possible to demonstrate that quinonemethides, generated by adduct decomposition, could alkylate AHQ^{-2}; this is shown by the reaction outlined in eq d, in which adduct 13 was formed by heating 29 in base at 100° in the presence of AHQ^{-2}.



29 9 13 (d)

Supporting evidence for the production of QM-AHQ adducts from QMs comes from the recent work of Landucci.[16] He has generated lignin-like quinonemethides in solution and observed their UV spectra prior to reaction with AHQ^{-2} to give adducts.

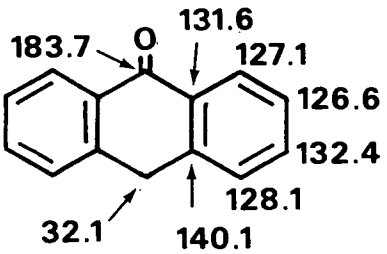
Carbon-13 NMR

Tables II and IV present the ^{13}C-NMR data for the various alkylated anthrones and anthrahydroquinones already discussed. Shown below are anthrone[22,25] and QM-AHQ adduct 14, with their ^{13}C-NMR assignments. The carbon numbering system is given with the structure shown on Table I.

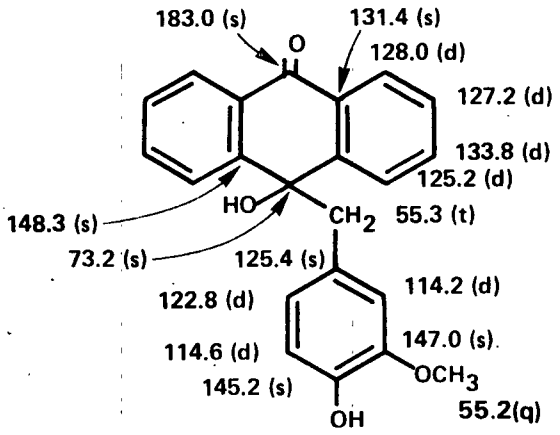
One would not expect substitution at C-10 to have much effect on the chemical shift positions of the upper part of the anthrone skeleton. Indeed, all the alkylated products showed C-1 (carbonyl) at 182.5 ± 1.0 (singlet), C-8a/C-9a at 131.0 ± 1.5 (singlet), C-1/C-8 at 128.0 ± 1.0 (doublet), C-2/C-7 at 126.7 ± 0.5 (doublet) and C-3/C-7 at 133.2 ± 1.0 PPM (doublet); these values correspond well with those of anthrone itself.

Replacement of one of the C-10 hydrogens of anthrone with a benzyl group, i.e., compounds 28 and 32, altered the chemical shifts of the lower portion of the anthrone ring in the following way: C-4/C-5 decreased from 128.1 to 125.6,

C-4a/C-10a increased from 140.1 to about 143 and C-10 increased from 32.1 to about 46 PPM. The downfield shifts can be explained by a positive polar effect exhibited by the substituent. The fact that the downfield shifts were not as large as would be calculated[37] and that C-4/C-5 experienced an upfield shift can be explained by a negative effect due to steric compression[37] as a result of the attached bulky substituent.



27



14

Placing both hydroxyl and alkyl substituents at C-10 caused the following changes in the anthrone chemical shifts: C-4/C-5 decreased from 128.1 to about 125.5, C-4a/C-10a increased from 140.1 to about 147 and C-10 increased from 32.1 to about 73 PPM. Acylation of the C-10 hydroxyl, i.e., 17, caused even more pronounced shifts, probably due to its greater withdrawing effect and greater bulk. The C-10 carbon was shifted considerably upfield in the cyclized product 41B.

If the C-10 substituent lacked symmetry and a sandwich structure (18) is assumed, one would expect that the two side rings of the anthrone skeleton in the adducts would exhibit different chemical shifts. This was, indeed, observed for the α-substituted benzyl substituted adducts 24, 25, 32 and 41B, which contained an asymmetric carbon, and the quinonemethide 31, which has cis/trans geometry. In several of these cases, the aromatic region was too complicated to make assignments, but the C-4a and C-10a carbons were observed as two distinct signals.

Interestingly, adduct 14 showed a simple spectrum even though the C-10 substituent here is dissymmetrical in a sandwiched conformation. This suggests that the π-complexed phenolic ring must undergo rapid bond rotations around the aryl-benzyl carbon such that the methoxyl group spends equal time over each side ring of the anthrone skeleton.

The chemical shift of the benzyl carbon of the C-10 benzyl substituent showed the expected variation[37] as a result of changes in the polar and steric effects of the other C-10 substituent. The chemical shifts of the other carbons of the C-10 benzyl and alkyl substituents agree well with predicted values[37] and models of similar structure.

Conclusions

Anthrahydroquinone and anthrone readily undergo reactions with conjugated ketones and aldehydes, of which quinonemethides are an example, to give addition products at the C_{10}-position. The adducts are characterized by existing (at least to some extent) in sandwich structures in which the C_{10}-substituent lies over the plane of the anthrone ring skeleton. Simple nonconjugated carbonyl electrophiles do not give stable addition products with AHQ^{-2}.

Mechanisms involving adduct intermediates of lignin quinonemethides and AHQ have been put forth to explain how AHQ promotes lignin fragmentation reactions.[7-10,14-16]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer model 700 Infrared Spectrometer and standardized with polystyrene. The ultraviolet spectra were obtained using a Perkin-Elmer 576 ST Spectrometer. A Joel FX 100 Spectrometer was used to obtain the NMR spectra. The NMR data given in Tables I-VI will not be repeated again in the Experimental Section. The mass spectra were obtained using a Hewlett-Packard model

598S GC-MS Spectrometer. Detailed analysis of the adducts' mass spectra will be treated elsewhere and not be repeated here.[28] Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois, and are reported in Tables I, III and VI.

Anthrahydroquinone. - Anthraquinone was stirred in an aqueous solution of 1 equivalent of sodium dithionite and 4 equivalents of sodium hydroxide under nitrogen at 60° for 45 min. The red colored solution was cooled, acidified with 10% hydrochloric acid and filtered by forcing the water out of the flask through a gas dispersion tube with nitrogen pressure. The resulting light green colored AHQ was washed 2-3 times by adding water to the flask, stirring briefly and filtering, as above. [This washing procedure was not necessary to obtain high yields of adducts from AHQ but did simplify the oxidative work-up procedure employed in the alkylations.]

Anhydrous AHQ was obtained by warming the flask containing the wet AHQ with a heat gun while applying a vacuum. The vacuum was broken by bleeding in nitrogen. Subsequent reactions employed the same flask. Aqueous AHQ^{-2}, which is deep red in color, was obtained by adding water containing 4 equivalents of sodium hydroxide to the wet AHQ.

General Alkylation Procedure. - The alkylating agent was added directly (no solvent) to an aqueous alkaline solution of 1.3 equivalents of AHQ^{-2} or anthrone monoanion (prepared from anthrone and excess sodium hydroxide), stirred for 1-3 hours at 60° under nitrogen and cooled to room temperature. Stirring in air converted the excess AHQ^{-2} and anthrone to AQ,[13] which was then removed by filtration. The filtrate was acidified and the precipitated product collected (depending on its state) by filtration or ether extraction, followed by drying (Na_2SO_4) and concentration. Product purification was generally accomplished by recrystallization.

4-Acetoxy-3-methoxybenzyl chloride (2). - The chloroacetate (2) was prepared (54.5% yield) from commercial vanillyl alcohol (Aldrich) according to the method of Taylor, et al.,[19] and recrystallized from ketone: mp 48-50°C; IR (neat) 1790 cm^{-1} (carbonyl); NMR and elemental analysis (Table VI).

Methanolysis of 4-Acetoxybenzyl chloride (1). - A solution of 1 gm of the chloroacetate (1)[19] in 25 mL anhydrous methanol, containing 1 drop of concentrated sulfuric acid, was stirred for 48 hours at room temperature. The reaction mixture was poured into 150 mL of water and the water solution was extracted with ether (3 x 30 mL). The ether layer was separated and washed with water, dried over anhydrous Na_2SO_4, and the solvent removed by evaporation in a nitrogen stream. The residue was a white crystalline material, mp 50-80°, showing no carbonyl absorption bands (IR) and a NMR spectrum ($CDCl_2$) showing 2.18 (s, 1, ?), 3.37 (s, 3, OCH_3), 4.38 (s, 2, CH_2), 5.91 (s, 1, OH), 6.74 (d, 2, J = 8 Hz, 3,5-aryl protons) and 7.18 δ (d, 2, J = 8 Hz, 2,6-aryl protons).

This reaction was also performed in a NMR tube. The chloroacetate (90 mg) was weighed into the tube and a 1:4 mixture of DMSO-d_6 and methanol added. A small drop of concentrated H_2SO_4 was added and spectra recorded at 5, 15, 40, 60 and 128 min. The reaction, as described above, to give ether 4 was complete after about 60 minutes; the spectra showed no other signals than those due to either 1 or 4.

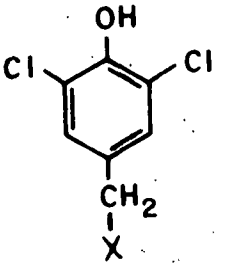
3,5-Dichloro-4-hydroxybenzyl Pyridium Chloride (12). - To a slurry of 5 gm of 4-hydroxy-α,2,6-trichlorotoluene (3),[19] mp 86-88.5°, in 10 mL of ether was added dropwise with stirring 50 mL of pyridine. A precipitate formed immediately and additional ether was added to aid the stirring. After only a few minutes, the reaction mixture was emptied into 3N HCl and extracted with ether. The ether extract was dried (Na_2SO_4) and concentrated to give 6.9 g (100%) of 12: mp 130-5°(d) (water); IR (mull) 2000-3700 cm^{-1} (phenolic and hydrated OH); NMR (Table V), also shows 3.4 δ (H_2O) signal.

Anal. Calcd for $C_{12}H_{10}Cl_3NO$: C, 49.65; H, 3.45; N, 4.83. Found: C, 44.51; H, 4.26; N, 4.28. Calcd for $C_{12}H_{14}Cl_3NO_2$ (dihydrate): C, 44.17; H, 4.29; N, 4.29.

3,5-Dichloro-4-hydroxybenzyl Methyl Ether (7). - The pyridine salt (12), 0.5 g, was dissolved in methanol (5 mL) and refluxed on a steam bath for 7 hours. A small

TABLE V

^{1}H-NMR ASSIGNMENTS FOR 3,5-DICHLORO-4-HYDROXYBENZYL DERIVATIVES[a]



	X = H	X = OH	X = Cl	X = OMe	X = 
Text no.		8	3	7	12
Solvent	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	DMSO
Aryl-OH	5.67 (s)	3.2-4.7[b]	5.86 (s)	5.91 (s)	10.60 (s)
Aryl-H	7.02 (s)	7.20 (s)	7.27 (s)	7.25 (s)	7.78 (s)
Benzyl	2.22 (s)	4.51 (s)	4.44 (s)	4.33 (s)	5.84 (s)
Other		OH 3.2-4.7[b]		Me 3.36 (s)	ortho 9.34 (d)[c]
					meta 8.17 (t)[c]
					para 8.62 (t)[c]

[a] Values are in δ units relative to TMS = 0.
[b] Very broad signal.
[c] J = 7-8 Hz.

amount of white precipitate formed. The methanol solution was diluted with water and extracted with ether; the ether was dried (Na_2SO_4) and concentrated. The residue was identified by ^{1}H-NMR as the methyl ether (7) (Table V).

3,5-Dichloro-4-hydroxybenzyl-Alchol (8). - A solution of 1.11 g of pyridine salt 12 in 55 mL of 1N NaOH was stirred at 80° for 1 day, cooled, acidified and extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated to afford alcohol 8: ^{1}H-NMR (Table V).

10-Hydroxy-10-(4'-hydroxy-3'-methoxybenzyl)-9(10H)-Anthracenone (13). - The adduct (13) was prepared (85% yield) by the reaction of 4-chloromethyl phenylacetate[19] with AHQ^{-2} according to the general procedure for AHQ reactions given above. The reaction was carried out in both water and 50% aqueous dioxane with reaction times varying from one minute to 3 hours. The same high yields (70-98%) were obtained in all cases. However, the yield of 13 was only about 2% (estimated by GC and NMR) when p-hydroxybenzyl alcohol (19) was reacted with AHQ^{-2} in the standard way. The properties of the adduct were: mp 224-8° (methanol); IR (mull) 3100-3500 (OH) and 1640 cm^{-1} (carbonyl); UV (ethanol) λ_{max} 277 (ε 12,300); elemental analysis and NMR (Tables I and II); mass spectrum reported elsewhere.[28]

10-Hydroxy-10-(4'-hydroxy-3'-methoxybenzyl)-9-(10H)-Anthracenone (14). - This adduct was prepared in high yield (82%) from the alkylation of AHQ^{-2} with chloroacetate 2 and low yield (estimated to be about 2% based on NMR and GC analysis)[28] from the alkylation of AHQ^{-2} with vanillyl alcohol (20). The standard alkylation procedure was used in each case. The properties of adduct 14 were: mp 161-5° (methanol-water); IR (mull) 3100-3600 (OH) and 1650 cm^{-1} (carbonyl); UV (ethanol) λ_{max} 272 (ε 12,700); elemental analysis and NMR (Tables I and II); mass spectrum.[28]

10-Hydroxy-10-(3',5'-dichloro-4'-hydroxybenzyl)-9 (10H)-Anthracenone (15). - The adduct 15 was prepared from AHQ^{-2} and either the pyridine salt 12 or 4-chloromethyl-2,6-dichlorophenol[19] according to the general procedure given above. The crude

product was obtained in 70% yield and was recrystallized from methanol/water: mp 198-208°C; IR (mull) 3100-3700 (OH) and 1640 cm^{-1} (carbonyl); UV (ethanol) λ_{max} 278 (ε 11,900); analysis and NMR (Tables I and II).

10-Hydroxy-10-(4'-acetoxybenzyl)-9(10H)-Anhracenone (16). - A mixture of 1.0 g of adduct 13, 2mL of acetic anhydride and 0.5 mL of pyridine was stirred under nitrogen at room temperature for 24 hours. The reaction mixture was diluted with water and extracted with ether. The ether extract was washed with saturated $NaHCO_3$ solution and then water, dried (Na_2SO_4) and concentrated to afford a colorless solid (16): mp 168-170° (toluene), IR (mull) 3400-3600 (OH), 1660 and 1715 cm^{-1} (carbonyls); elemental analysis and NMR (Tables I and II).

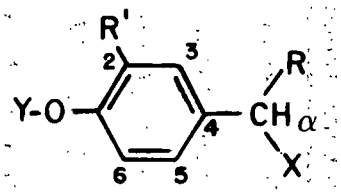
10-Acetoxy-10-(4'-acetoxybenzyl)-9(10H)-anthracenone (17). - A mixture of 0.8 g of adduct 13, 2mL of acetic anhydride and 0.5 mL of pyridine was stirred under nitrogen at 95° for 24 hours. After cooling, the reaction mixture and a little wash ether were emptied into dilute HCl. Agitation produced a precipitate (0.71 g, 68%) of 17: mp 167-8° (toluene); IR (mull) 1660, 1740 and 1760 cm^{-1} (carbonyl groups); elemental analysis and NMR (Tables I and II); mass spectrum.[28]

1-Chloro-1-(4'-acetoxy-3'-methoxyphenyl)ethane (22). - Chloroacylation[19] of α-methyl vanillyl alcohol,[38] mp 91-93°, afforded after vacuum distillation a 79% yield of 22: bp 124-7°/1 mm; IR (neat) 1760 cm^{-1} (carbonyl); elemental analysis and NMR (Table VI).

1-Chloro-1-(4'-acetoxy-3'-methoxyphenyl)propane (23). - First, 1(4-hydroxy-3-methoxyphenyl)-1-propanol was prepared according to the method of Zentner[39] and recrystallized once from toluene and twice from chloroform, mp 78-79.5°C. This material was then chloroacylated according to the procedure of Taylor, et al.,[19] and vacuum distilled to afford (65% yield) compound 23: bp 125-6°/1 mm; IR (neat) 1760 cm^{-1} (carbonyl); elemental analysis and NMR (Table VI).

TABLE VI

^{1}H-NMR ASSIGNMENTS AND ELEMENTAL ANALYSES OF SOME QUINONEMETHIDE PRECURSORS[a,b]



Text No.	Solvent	X	Y	R	R^1	C-6	C-5	C-3	C-α	Calculated (Found)[e] %C	%H
1	$CDCl_3$	Cl	$COCH_3$	H	H					--	--
			2.27 (s)		7.05 (d)		7.38 (d)		4.51 (s)		
2	$CDCl_3$	Cl	$COCH_3$	H	OCH_3					55.94 (56.03)	5.13 (5.14)
			2.30 (s)		3.84 (s)		6.7-6.9 (m)		4.56 (s)		
4	$CDCl_3$	OCH_3	H	H	H					--	--
		3.37 (s)	5.91 (s)		6.74 (d)		7.18 (d)		4.38 (s)		
	DMSO	OH	H	CH_3	OCH_3					--	--
		4.94 (d)[c]	8.68 (s)	1.27 (d)	3.74 (s)		6.7-6.9 (m)		4.5 (d of q)[c]		
22	$CDCl_3$	Cl	$COCH_3$	CH_3	OCH_3					57.77 (58.18)	5.69 (5.87)
			2.25 (s)	1.80 (d)	3.79 (s)	7.07 (s)		7.22 (s)	5.23 (q)		
	$CDCl_3$	OH	H	CH_2CH_3	OCH_3					--	--
		1.89 (s)	5.63 (s)	1.73 (m) 0.90 (t)	3.38 (s)		6.7-6.9 (m)		4.51 (t)		
23	$CDCl_3$	Cl	$COCH_3$	CH_2CH_3	OCH_3					59.38 (59.65)	6.19 (6.24)
			2.28 (s)	2.06 (p)[d] 1.00 (t)	3.81 (s)		6.9-7.0 (m)		4.74 (t)		

[a] Values are in δ units relative to TMS = 0.
[b] The coupling constants, J, were all in the 7-9 Hz range unless noted otherwise.
[c] Doublet has J = 4Hz.
[d] p = pentet.
[e] Analyses are only given for those compounds which have not been reported in the literature.

10-Hydroxy-10-(4'-hydroxy-3'-methoxy-α-methylbenzyl)-9(10H)-anthracenone (24). - Employing the standard alkylation procedure, chloroacetate 22 and AHQ^{-2} afforded an 87% yield of a complex product mixture. The crude product was applied to a silica gel column (EM 60) and eluted with hexane, combinations of hexane and chloroform, pure chloroform and finally methanol. The three fractions which were eluted with chloroform were combined and rechromatographed on a silca gel column (EM 60) and eluted with chloroform, combinations of chloroform and ether, pure ether and finally methanol. The adduct (24) was obtained (10% yield) from the eight fractions which eluted with the 10% ether/chloroform solvent mixture: IR (neat) 3100-3700 (OH), and 1660 cm^{-1} (carbonyl); the NMR (Tables III and IV) displayed a few minor impurities; mass spectrum.[28]

10-Hydroxy-10-(4'-hydroxy-3'-methoxy-α-ethylbenzyl)-9(10H)-anthracenone (25). - Anthrahydroquinone dianion was alkylated with chloroacetate 23 in the standard manner, as described above, using an ether extraction isolation procedure. The crude product was then placed in a few mLs of ether. A small amount of insoluble yellow crystals of 25 was collected by filtration: NMR (Tables III and IV). The filtrate was chromatographed on a silica gel (EM 60) column, eluted with hexane, hexane/chloroform, chloroform, chloroform/ether and ether. ^{1}H-NMR spectra of the fractions resulting from this chromatography showed a mixture of products, one of which was the adduct (25). The yield of (25) was estimated to be 25%.

Alkylation of Anthrone (27) with p-acetoxybenzyl Chloride (1). - The di-substituted alkylation product, 10,10-di-(4'-hydroxybenzyl)-9(10H)-anthracenone (29), was prepared in good yield (98%) by reacting 1 equivalent of anthrone (27) with 2 equivalents of chloroacetate 1, using the general alkylation procedure, 50% aqueous dioxane and 2 hours at 95°. The product was recrystallized from methanol/water: mp 211-214°C, IR (mull) 3100-1700 (OH) and 1630 cm^{-1} (carbonyl), NMR and elemental analysis (Tables III and IV).

The mono-alkylated product, 10-(4'-hydroxybenzyl)-9(10H)-anthracenone (28), was prepared in the same manner as 29 above only using 1 equivalent of chloroacetate 1. The crude product, isolated by chloroform extraction of the acidified reaction mixture, was a complex mixture of components, one of which was the dialkylated product 29. The chloroform residue was worked up by a series of rather complicated recrystallizations involving several different types of solvents. Anthraquinone was isolated in several of the steps, indicating that the product mixture was probably decomposing. Briefly, the product was taken up in toluene; that which did not dissolve was largely AQ, but contained some 10-methoxy-10-(4'-hydroxybenzyl)-9(10H)-anthracenone (30). The latter was separated from the AQ by washing with ethanol, evaporation and recrystallization from methanol; mp 132°(d); IR 2800-3500 (OH), 1650 cm^{-1} (carbonyl), NMR and elemental analysis (Tables III and IV).

The toluene soluble material was concentrated to give a gummy solid and a filtrate. The gummy solid was a mixture of AQ and a material of mp 170-173°C (from MeOH), whose ^{1}H-NMR spectrum changed upon standing; no structural assignment was made.

A ^{1}H-NMR spectrum of the toluene filtrate (concentrated) indicated the presence of the desired alkylation product (28). This material was chromatographed on a silica gel (EM 60) column, eluted with hexane, hexane/chloroform, chloroform and methanol. The desired product (28) was identified by ^{1}H-NMR in several fractions which eluted with 50% chloroform/hexane. Further attempts to purify the product by recrystallization from methanol/water were unsuccessful. The NMR spectral data for 28 is given in Tables III and IV. The elemental analysis (Table III) of the chromatographed product indicated the sample was not completely pure; the NMR spectra were, however, quite clean - the only significant impurity appeared to be water. The mass spectrum[28] also supported the proposed structure 28.

Dehydration of Adduct 13 to Give 31. - A mixture of 1.0 g of 13, 0.6 g of p-toluenesulfonic acid and 30 mL of toluene was refluxed for 2 hours, cooled and extracted with aq. $NaHCO_3$. The separated toluene phase was dried (Na_2SO_4) and evaporated to give 0.9 g (95%) of orange solid (31): mp 139-141° (DMSO-water); IR (mull) 2600-3400 (hydrated ArOH) and 1660 cm^{-1} (carbonyl); NMR (Tables III and IV); elemental analysis of dried sample (Table III). Drying in an oven at 105° overnight changed the melting point to about 190°(d), but did not have much effect on the spectral properties.

10-(4'-hydroxy-3'-methoxy-α-methylbenzyl)-9(10H)-anthracenone (32). - Anthrone (27), 3.0 g (15.4 mmoles) was stirred with chloroacetate 22, 3.9 g (17 mmoles) and NaOH (4.2 g) in 200 mL of 50% aqueous dioxane under nitrogen while warming the mixture from room temperature to 95°C over 2 hours. The reaction mixture was stirred 1/2 hour longer at 95°C then cooled, stirred in air for 5 min. and filtered to remove AQ. The filtrate was diluted with water and acidified with concentrated hydrochloric acid. The crude product was separated from residual AQ by methanol washing. The residue from evaporation of the methanol was dissolved in ether, dried (Na_2SO_4) and evaporated. The resulting amber colored viscous liquid was purified by column chromatography using silica gel (EM 60) and eluting with hexane, chloroform-hexane mixtures, chloroform and methanol. Fractions eluting with 50-70% chloroform-hexane contained 32: IR (neat) 3150-3650 (OH) and 1660 cm^{-1} (carbonyl); NMR (Tables III and IV); mass spectra (as is and derivatized with dimethylsulfate) are reported elsewhere.[28] Attempts to recrystallize 32 failed. The estimated yield was 65%.

Methylation of Adducts. - Adducts 13, 14, 28, 29 and 32 were methylated with dimethyl sulfate[28] and analyzed by GC/MS. The products were principally the dimethylated derivatives, contaminated by small amounts of decomposition by-products resulting from the alkali and THF used in the derivatization procedure.[28] An exception was adduct 28, which was nearly totally destroyed by the derivatization procedure. The mass spectra are discussed elsewhere.[28]

10-Hydroxy-10-benzyl-9(10H)-anthracenone (37). - Benzyl chloride was reacted with AHQ^{-2} under the standard conditions; the product 37, not being a phenol, was precipitated along with the AQ. The precipitate was washed several times with ether to solubilize 37 and leave behind AQ, which is relatively insoluble in ether. The combined ether washings were dried (Na_2SO_4) and evaporated to afford (59% yield) a pale yellow solid (37), which turned pink upon standing in air: mp 144-6° (hexane/toluene); IR (mull) 3200-3500 (OH) and 1660 cm^{-1} (carbonyl); elemental analysis and NMR (Tables III and IV).

10-Hydroxy-10-(3'-oxobutyl)-9(10H)-anthracenone (40A). - A procedure identical to that used to prepare 37 was employed, the only exception was that the alkylating agent was methyl vinyl ketone (38). The crude product was purified by column chromatography, employing silica gel (EM 60) and eluting with hexane, 50:50 hexane-chloroform, chloroform, 50:50 chloroform-THF and dioxane. The major portion of the product (54% yield) was eluted with the 50:50 chloroform-THF solvent mixture: 40A was a colorless solid; mp 99-102° (methanol-water); IR (mull) 3150-3800 (OH), 1710 and 1660 cm^{-1} (carbonyls); elemental analysis and NMR (Tables III and IV).

10-Hydryoxy-10-(1'-phenyl-3-oxopropyl)-9(10H)-anthracenone Hemiacetal (41B). - Freshly distilled cinnamaldehyde (39) was reacted with AHQ^{-2} under the standard conditions. The work-up, however, involved quenching the cool reaction mixture with dilute hydrochloric acid, under nitrogen, filtering in air and separating the product from AQ by exhaustive extraction with ether using a Soxhlet extractor. The ether solution was dried (Na_2SO_4) and evaporated to give 41B in 38% yield: mp 201-205° (methanol); IR (mull) 3100-1800 (OH) and 1660 cm^{-1} (carbonyl); elemental analysis and NMR (Tables III and IV).

Quinonemethide Transfer from 29 to AHQ^{-2}. - A mixture of 1.5 g of 10,10-di(4'-hydroxybenzyl)-9(10H)-anthracenone (29) and 4 equivalents of AHQ^{-2} was stirred at 60° for 4 hours, cooled, exposed to air (until the red color diappeared), and

filtered to remove the excess AQ. The filtrate was acidified and the precipitate collected by filtration. Analysis of the product mixture by ^{1}H-NMR and GC-MS (after derivatization)[28] showed that the major components were starting material 29, adduct 13 and AQ; there was no evidence for the presence of monoalkylated anthrone adduct 28.

References

1. J. P. Casey, "Pulp and Paper Chemistry and Chemical Technology," 3rd Ed., Vol. I, Wiley-Interscience, N.Y., 1980.
2. H. H. Holton, Pulp Paper Can., 78, T218 (1977).
3. B. I. Fleming, G. J. Kubes, J. M. MacLeod, and H. I. Bolker, Tappi, 61 (6), 43 (1978).
4. W. H. Algar, A. Farrington, B. Jessup, P. F. Nelson, and N. Vanderhoek, Appita, 33, 33 (1979).
5. J. R. Obst, L. L. Landucci, and N. Sanyer, Tappi, 62 (1), 55 (1979).
6. J. Nakano, et al., Japan Tappi, 33, 410, 666 (1979); J. Jap. Wood Res. Soc., 25, 239 (1979).
7. H. Aminoff, G. Brunow, G. E. Miksche, and K. Poppius, Paperi Puu, 61, 441 (1979).
8. J. Gierer, O. Lindeberg, and I. Noren, Holzforschung, 33, 213 (1979).
9. D. Dimmel, D. Shepard, T. Brown, and R. McKelvey, 1979 Canadian Wood Chemistry Symposium, Harrison Hot Springs, British Columbia, Canada, September 19-21, 1979.
10. J. S. Gratzl, EUCEPA Sym., Paper No. 12, Helinski, June 2-5, 1980.
11. B. I. Fleming, G. J. Kubes, J. M. MacLeod, and H. I. Bolker, Tappi, 62 (7), 55 (1979).
12. A. Farrington, P. F. Nelson, and N. Vanderhoek, Appita, 32, 300 (1979).
13. F. Arbin, L. Schroeder, N. Thompson, and E. Malcolm, Tappi, 63 (4), 152 (1980).
14. D. R. Dimmel, and D. Shepard, ACS Meeting, Cell. Division, Las Vegas, Aug. 25, 1980.
15. L. L. Landucci, ACS Meeting, Cell. Division, Las Vegas, Aug. 25, 1980.
16. L. L. Landucci, Tappi, 63 (7), 95 (1980).
17. O. Samuelson, Pulp & Paper Canada, 81, 68 (1980).

18. J. Martin in "Lignins," K. V. Sarhanen and C. H. Ludwig Editors, Wiley Interscience, N. Y., 1971, Chapter 16.

19. L. D. Taylor, J. M. Grasshoff, and M. Pluhar, J. Org. Chem., 43, 1197 (1978).

20. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd Ed., Wiley-Interscience, 1966, p. 551.

21. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric identification of organic compounds," 3rd Ed., John Wiley and Sons, Inc., N. Y., 1974, p. 175.

22. O. R. Gottlieb, et al., Phytochem., 16, 735 (1977).

23. Y. Berger and A. Castonguay, Org. Magn. Reson., 11, 375 (1978).

24. A. Arnone, G. Fronza, R. Mondelli, and J. St. Pyrek, J. Magn. Reson., 28, 69 (1977).

25. J. L. Marshall, A. M. Ihrig, and D. E. Miller, J. Magn. Reson., 16, 439 (1974).

26. A. Farrington, P. E. Nelson, and N. Vanderhoek, Appita, 33, 248 (1979).

27. J. March, "Advanced Organic Chemistry," 2nd Ed., McGraw-Hill, N.Y., 1977, p.79-82 and references cited therein.

28. D. R. Dimmel and D. Shepard, J. Wood Chem. Technol., submitted for publication.

29. L. J. Filar, and S. Winstein, Tetrahedron Letters, 9 (1960).

30. G. Leary and W. Thomas, Tetrahedron Letters, 3631 (1975).

31. G. Leary, I. J. Miller, W. Thomas, and A. D. Woolhouse, J.C.S. Perkin II, 1737 (1977).

32. T. J. Fullerton and B. I. Fleming, Svensk Papperstid., 83, 396 (1980).

33. G. A. Russell, et al., and Hawthorne, et al., in "Oxidation of Organic Compounds," Vol. I., Adv. in Chem. Series 75, American Chemical Society, 1968, p. 184, 203-215.

34. R. J. Deshpande, Indian J. Chem., 16B, 389 (1978).

35. T. J. Fullerton and S. P. Ahern, J.C.S. Chem. Commun. 457 (1979).

36. D. W. Cameron and E. L. Samuel, Tetrahedron Letters, 3035 (1979).

37. G. C. Levy, R. L. Lichter and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance Spectroscopy," 2nd Ed., Wiley-Interscience, N.Y., 1980, Chapters 2-4.

38. C. W. Baily and C. W. Dence, Tappi, 52 (3), 498 (1969).

39. T. G. Zentner, Doctoral Thesis, The Institute of Paper Chemistry, Appleton, WI (June 1952).